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Feature article

High-strength, translucent glass-ceramics in the system
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ABSTRACT

In a MgO/Al₂O₃/SiO₂/ZrO₂ glass-ceramic MgO was substituted by equimolar ZnO concentrations. The effect of this substitution on the crystallization behavior, the microstructure and the mechanical properties of the glass-ceramics was studied. The crystal phases and the microstructure were analysed by X-ray diffraction and scanning electron microscopy. Tetragonal ZrO₂, a high-/low-quartz solid solution (high-/low-QSS) and spinel/gahnite were observed in the entire bulk of the glass-ceramics. Additionally, indialite or cristobalite are detected at the surface of some glass-ceramics. The substitution of small ZnO concentrations induces an increasing low-QSS concentration and hence higher microhardness and Young's modulus. By contrast, higher ZnO concentrations lead to a liquid/liquid phase separation in the glass. Moreover, spinel/gahnite is the main crystal phase and the concentration of the low-QSS is smaller in these glass-ceramics which also do not show as good mechanical properties. However, the biaxial flexural strength of the glass-ceramics is not notably affected by the ZnO concentration.

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1. Introduction

Glass-ceramics in the MgO/Al₂O₃/SiO₂ (MAS) [1–15] and MgO/ZnO/Al₂O₃/SiO₂ (MZAS) systems [4–6,17–21] have frequently been studied in the past few years. They are reported to show excellent microwave properties [12–14,16,17] and also excellent mechanical properties [1,4–9,15,17,20], such as Young's moduli of up to 147 GPa [4], hardness of up to 13 GPa [4–6] and mechanical strengths of up to 475 MPa [5,6]. Hence, glass-ceramics in this system offer a large variety of novel fields of application, e.g. for electronic packaging devices [1,17], as millimeter-wave dielectrics [12–14] or as hard disk substrates [15,21].

The stoichiometric cordierite composition in the MAS base glass system shows exclusively surface crystallization, here mainly μ -cordierite (also denoted as high-quartz solid solution [23] or β -quartz solid solution [20,21]) or, however, indialite is formed [22–25]. The μ -cordierite is stable at temperatures <950 °C and transforms irreversibly to indialite above this temperature [26]. By contrast, adding nucleating agents such as TiO₂ [1–4] or ZrO₂ [3–11] leads to volume crystallization and to the formation of a fine

grained microstructure. Purple to blue colored glass-ceramics are observed if TiO₂ [1] is used, while ZrO₂ is the favorable nucleating agent if colorless glass-ceramics are required [6].

The formation of finely dispersed crystal phases with relatively high coefficients of thermal expansion (CTE), e. g. the low-quartz solid solution (low-QSS, CTE_{20–300 °C} = 13.2 × 10^{−6} K^{−1} [27]), spinel (CTE_{20–800 °C} = 8 × 10^{−6} K^{−1} [27]) or tetragonal ZrO₂ (CTE_{tetragonal} = 10.5 × 10^{−6} K^{−1} [28]), is advantageous for high-strength glass-ceramics, due to remarkable stresses in the microstructure after cooling which result in excellent mechanical properties [2,6,7]. Thermal treatment of glasses containing ZrO₂ concentrations > 5.7 mol% at temperatures of ca. 950 °C, first leads to the crystallization of tetragonal ZrO₂ followed by the precipitation of a high-quartz solid solution (high-QSS) [6,10] which typically contains ca. ≥ 10 mol% of each MgO and Al₂O₃ [29]. These oxides stabilize the high-QSS during cooling to room temperature (RT) and prevent the phase transition to the low-QSS [2,6,29]. Longer annealing times and annealing temperatures ≥ 1000 °C result in the depletion of MgO and Al₂O₃ in the high-QSS to concentrations as low as 1–2 mol%. This leads to the crystallization of spinel (MgAl₂O₄) and to the transformation of the high-QSS to the low-QSS during cooling to RT [6,10,29]. In pure quartz, this phase transformation runs parallel to a decrease in volume of 0.8% [4] which occurs at 573 °C [30]. In the present glass system, the transformation occurs at 480–530 °C [2]. Due to the volume contraction

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Table 1
Prepared glass compositions in mol%.

Sample	A	B	C	D
SiO ₂	51.0 mol%	51.0 mol%	51.0 mol%	51.0 mol%
Al ₂ O ₃	20.8 mol%	20.8 mol%	20.8 mol%	20.8 mol%
MgO	20.8 mol%	18.2 mol%	15.6 mol%	10.4 mol%
ZnO	–	2.6 mol%	5.2 mol%	10.4 mol%
ZrO ₂	7.4 mol%	7.4 mol%	7.4 mol%	7.4 mol%

during the phase transformation, notable stresses occur in the microstructure, which also lead to the good mechanical properties. The phase transformation from the high-QSS to the low-QSS can be detected by a slight shift of the peak positions in X-ray patterns and in dilatometric curves [2,3]. Annealing at even higher temperatures of ca. 1200 °C may also lead to the formation of high-cristobalite [2] which shows a phase transition to low-cristobalite during cooling at temperatures in the range from 180 to 270 °C [30]. This transition is accompanied by a steep decrease in volume of ca. 2.8 % which together with its very high CTE (CTE_{20–300 °C} = 50 × 10^{−6} K^{−1} [27]) results in high stresses and often in the destruction of the material [3].

However, melting of these MAS glasses requires high temperatures which can be slightly decreased by adding components such as P₂O₅ [31] or B₂O₃ [32]. The addition of ZnO also decreases the viscosity and the glass transition temperature T_g of the glass [4,5]. The mechanical properties of the glass-ceramics are nearly as good as those of the ZnO-free glass-ceramics [4–6]. Furthermore, glass-ceramics in the MZAS system with ZrO₂ as nucleating agent show high translucency [20]. In analogy to MgO, ZnO can also be incorporated into the high-/low-QSS [4,5]. Moreover, the addition of ZnO and MgO leads to the formation of MgAl₂O₄ (spinel)/ZnAl₂O₄ (gahnite) solid solutions [4–6].

In this paper, a study on the system MgO/ZnO/Al₂O₃/ZrO₂/SiO₂ is presented. A part of the MgO concentration is replaced by equimolar concentrations of ZnO, which should result in a decrease of the required melting temperature. In contrast to other components such as P₂O₅ or B₂O₃, hardness, strength and elastic modulus should not be decreased in a notable extend [4–6]. The crystallization behavior is mainly investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). In addition to the mechanical properties, the optical properties of the glass-ceramics are studied which might be interesting for diverse fields of application.

2. Materials and methods

2.1. Preparation of the glasses and glass-ceramics

Table 1 shows the chemical compositions of the prepared glass-ceramics. Starting from composition A with 20.8 MgO/20.8 Al₂O₃/51.0 SiO₂/7.4 ZrO₂ (in mol%), a portion of 1/8, 1/4 or 1/2 MgO was replaced by equimolar concentrations of ZnO in the compositions B to D.

The glasses were melted from the reagent grade raw materials SiO₂ (quartz), 4 MgCO₃·Mg(OH)₂·5 H₂O, ZnO, Al(OH)₃ and ZrO₂. The raw materials for batches of 300 g glass were mixed and then melted in a middle frequency furnace in a covered platinum/rhodium 20 crucible at temperatures of 1590–1630 °C. The melt was stirred for 2 h with a frequency of 60 min^{−1} to improve the homogeneity. After casting the melt on a steel mould preheated to 600 °C, the glass was placed in a muffle furnace preheated to 800–830 °C. Then the furnace was switched off to allow the glass to cool with a rate of ca. 2–3 K min^{−1} to room temperature.

Subsequently, the glasses were cut into pieces for the respective investigations. Glass-ceramics were produced by thermal treat-

ment at 1050 or 1100 °C for 3 h (Nabertherm N11/H) using heating and cooling rates of 5 K min^{−1}.

2.2. Thermal properties and density

To determine the crystallization temperatures of the glasses, the glasses were powdered to a grain size fraction of 250–315 μm and analysed by differential thermal analysis (DTA) using a Shimadzu DTA-50. The supplied heating rate was 5 K min^{−1} and the error of the temperature is approximately ± 5 K.

Dilatometric measurements were performed to investigate the glass transition temperatures T_g , the dilatometric softening points T_s and the CTE of the glasses. For dilatometry, glass specimens with a diameter of 8 mm and a length of 25 mm were analysed by a NETZSCH Dil 402 PC using a heating rate of 5 K min^{−1}. The error of the CTE is ca. ± 0.1 · 10^{−6} K^{−1} and the temperature error is approximately ± 5 K.

The glass densities were determined by a helium pycnometer AccuPyc 1330 (Micromeritics). The error of the density is ca. ± 0.001 g cm^{−3}.

2.3. Phase composition and microstructure

X-ray diffraction (XRD) was used to ensure that the melted glass specimens are amorphous. For this purpose, the glasses were powdered and subsequently analysed. Furthermore, the phase composition of compact glass-ceramics (not powdered) was studied by XRD in a Siemens D5000 diffractometer. The patterns were recorded with CuK_α radiation (λ = 0.154 nm) using a step width of 0.02° in a 2θ-range from 10 to 60°. The most intense peak of each pattern was normalized to 100% for a better comparison of the patterns.

A scanning electron microscope (SEM) JEOL JSM 7001F was used to study the microstructure of the glass-ceramics. The conductivity of the samples was achieved by mounting the samples using Ag paste and coating them with a thin carbon layer.

Moreover, transmission electron microscopy (TEM) was used to analyse the homogeneity of the glasses with a HITACHI H8100 TEM using an acceleration voltage of 200 kV. Replica micrographs of fractured surfaces, which were etched in a mixture of hydrofluoric (5%) and nitric acid for 10 s, were taken.

2.4. Contrast ratio (CR)

The CR of the glass-ceramics was analysed using an L*a*b*-spectrometer of the type CM-3700d (Konica-Minolta). The samples were prepared according to BS5612. The translucency of a material decreases with increasing CR value.

2.5. Mechanical properties

The Vickers hardness H_V (microhardness) and the indentation fracture toughness K_{1C} of coplanar, polished glass and glass-ceramic samples was measured using a microhardness tester Duramin 1 (Struers). For the determination of the microhardness H_V , ten indentations with a load of 1.96 N spaced over the entire samples were made. Eq. (1) was used to calculate the microhardness H_V [33]:

$$H_V = 1.854 \cdot \frac{F}{d^2} \quad (1)$$

where F is the supplied force in N and d is the mean length of the indentation diagonals in m.

The supplied load for the measurement of the indentation fracture toughness K_{1C} was 9.81 N. Ten indentations were performed

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